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Characterization of Polycyclic Aromatic Hydrocarbons (PAH) and Nitro-PAH Emissions from HDDV with PM and NO_X Controls

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) and nitro-PAHs consist of many toxic compounds which could be carcinogenic or mutagenic such as benzo(a) pyrene or 1-nitro-pyrene. The lighter PAHs (predominantly in vapor phase) are the most abundant in the urban atmosphere and may react with other pollutants to form more toxic derivatives. Motor vehicles are a significant contributor to ambient PAH emissions. The stringent PM and NO_X diesel emission standards force manufactures to modify diesel engines and/or retrofit them with advanced emission control devices such as particle traps and selective catalytic reduction (SCR) technology. These aftertreatment devices have proven effective in reducing PM and NO_X and also changes the physicochemical properties of diesel exhaust. It is expected that PAH and nitro-PAH profiles of diesel exhaust could be altered by the aftertreatment devices as well. However, this effect has not yet been fully investigated.

This project is a 4-year collaborative research effort focused on emerging issues relevant to air quality and the protection of health[1]. These issues include: 1). ultralow emissions from advanced aftertreatment technology, 2). effects on emissions of ultrafine and nucleation mode particles by various aftertreatment devices, 3). measurement instrumentation and protocols, and 4). the relative toxicity of PM components as a function of volatility.

In this study, four heavy-duty diesel vehicles (HDDV) of 1998 to 2007 vintage, operating with advanced PM and/or NO_X emissions control retrofits were tested on a heavy-duty chassis dynamometer located at ARB's Heavy-duty Diesel Emissions Test Laboratory (HDETL) in Los Angeles. The emissions control retrofits included four diesel particulate filters (DPF), catalyzed and un-catalyzed, and two prototype SCR systems. The combination of DPF and SCR technologies are of particular interest because they may represent the future approach for simultaneous control of PM and NO_X.

METHOD

Teflon coated glass fiber filter in series with XAD adsorbent was used to collect PM and vapor-phase pollutants respectively for the analysis of semi-volatile PAHs, volatile PAHs, and nitro-PAHs. One challenge in analyzing PAHs and especially nitro-PAHs is the low mass emissions of these species and the laboratory analytical detection limits. Vapor phase PAHs were analyzed using 5-point calibration curves with the isotope dilution standard method [2]. For nitro- and dinitro-PAH analysis, deuterated internal standards 2-nitrodiphenyl-d9 and 1-nitropyrne-d9 were added to the filters, and the filters were then extracted with dichloromethane using the Dionex ASE300 followed by acetone extraction. The extracts were further precleaned by the solid-phase extraction technique and semi-preparative normal-phase high performance liquid chromatography (HPLC) technique (Waters). The fraction corresponding to nitro- and dinitro-PAH was collected and analyzed by negative ion chemical ionization (NICI) gas chromatography – mass spectrometry (GC/MS) [3].

Research Team

Air Resources Board, UCLA, UC DAVIS, USC

Co-sponsors:

California Energy Commission, SOUTH COAST AQMD

Principal in-kind contributors:

DART, CALIFORNIA DEPARTMENT OF TRANSPORTATION, RTD, bp

Figure 1 – Tested Vehicles and Naming Convention

Veh#1 –Class 8 tractor. Tested as a baseline, with a JM CRT®, SCR* (vanadium and zeolite). Baseline, DPF1, DPF1+SCR1, DPF1+ SCR2

Veh#2 - CalTrans Truck with Engelhard DPX (Catalyzed DPF). DPF2

Veh#3 – School Bus with a Cleaire Horizon electrically regenerated Trap. DPF3

Veh#4 –Diesel Hybrid Electric Bus with JM CCRT®. Cruise and Idle not tested. DPF4

*** Prototype systems, not commercial units**

Figure 2 – CARB HDETL

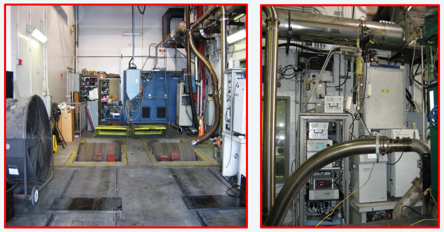
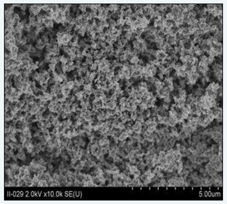
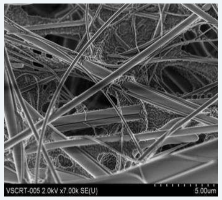


Figure 3 – TEM Image of diesel particles from baseline and retrofit collected on fibrous filters



Baseline, agglomerate



DPF1+SCR1, Clean as blank

*** Filter Sample Micrographs Courtesy of D. Su, Fritz-Haber Institute**

RESULTS

Figure 3 shows the TEM image of the diesel particles from the Baseline and DPF1+SCR1 vehicles collected on fibrous filters. Particles from the Baseline are agglomerates. Those agglomerate are barely seen in the sample from DPF+SCR1.

Figure 4 shows the volatile and particle phase PAH emissions from the Baseline diesel truck without emission controls. The volatile PAHs account for 98% of the total PAHs (volatile + particulate phase), and the light molecular weight (MW) PAHs, 2- and 3-ring, dominates the volatile PAHs. Naphthalene accounts for 80% of the volatile PAHs.

Figure 5 shows the sum of the volatile and particulate PAHs from the retrofits during cruise cycle. The retrofits reduce both particle and vapor phase PAHs by more than 90%. The retrofits reduce particle phase PAHs by more than 95%, independent of the driving cycle and catalytic loadings, which implies that reduction of particle PAHs is by direct removal in the trap. The uncatalyzed DPF was less efficient in reducing the volatile PAHs compared to the catalyzed DPFs **(Figure 6).**

Figure 7 shows selected nitro-PAHs from the test vehicles. Results demonstrate that SCRs did not promote formation of nitro-PAHs. DPF2 and DPF3 show significant reduction of 1-nitropyren but slightly increase of 3-nitrophenanthrene.

Figure 4 – Individual volatile and particle phase PAHs emissions from Baseline

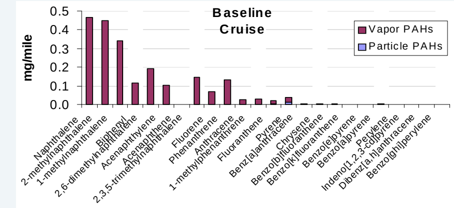


Figure 5 – Total (volatile + particle phase) PAHs emissions from Baseline and retrofits.

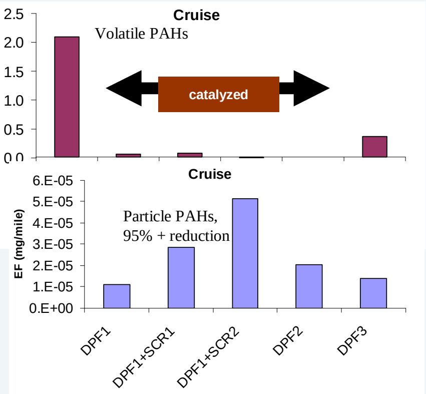
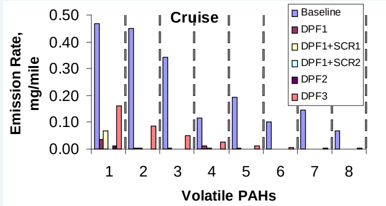


Figure 6 – Selected volatile PAHs emissions.



(1). Naphthalene ; (2). 2-Methylnaphthalene; (3). 1-Methylnaphthalene; (4). Biphenyl; (5). 2,6-Dimethylnaphthalene; (6). Acenaphthylene; (7). 2,3,5-Trimethylnaphthalene; (8). Fluorene

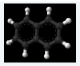
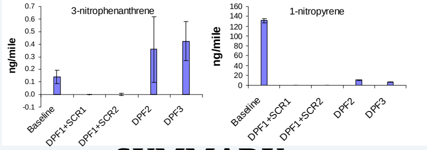


Figure 7 – Selected nitro-PAHs emissions.



SUMMARY

Retrofits reduce total PAHs (particle and vapor phase) by more than 90%. The particle phase PAH reduction are independent of the catalytic surface and driving conditions. However, vapor phase PAHs are highly affected by catalytic loadings and exhaust temperature [1]. With a few exceptions, most of the samples from retrofitted engines do not contain nitro-PAHs. The 1-nitro-pyrene is the most dominant nitro-PAH. The engine without retrofits show one order of magnitude higher emissions of 1-nitro-pyrene than engines with uncatalyzed DPF and catalyzed DPF. The uncatalyzed DPF shows higher emission of 3-nitrophenanthrene than the baseline. The two prototype SCRs did not promote the nitration of PAHs. Significant reduction of 1-nitropyrene, a recognized carcinogen, suggests direct benefit of DPF for cancer risk reduction.

Acknowledgements

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Reference

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2. Kado, N., et al., *Environ Sci Technol* **2005,** *39,* 7638-7649.
3. Zielinska et al., *Atmos. Environ.*, **1989,** 23, 223-229.

See also at AAAR

10F.4 Friday 12:00 am: The effect of diesel particulate filters and selective catalytic reduction-A predictive framework for ultrafine particle formation, toxicity and chemical composition.